Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 1

8872/02

Paper 2

16 August 2016
2 hours

Candidates answer Section A on the Question Paper

Additional Materials: Writing Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

The use of an approved scientific calculator is expected, where appropriate.

Section A
Answer **all** the questions.

Section B
Answer **two** questions on separate answer paper.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Question no.	**Marks**
Section A	
B4	
B5	
B6	
TOTAL	

This document consists of **16** printed pages.

Section A

Answer **all** questions in this section in the spaces provided.

1 The element chromium was discovered in 1797 by French chemist Louis Nicolas Vauquelin. A number of naturally occurring isotopes of chromium have been identified as listed below.

isotope	relative isotopic mass	natural abundance (%)
^{50}Cr	49.95	4.34
^{52}Cr	51.94	83.79
^{53}Cr	52.94	9.50
^{54}Cr	53.94	2.37

(a) Use the above data to calculate the relative atomic mass of chromium to two decimal places.

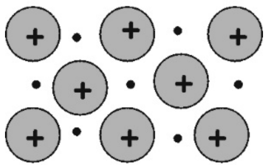
[(49.95)(4.34) + (51.94)(83.79) + (52.94)(9.50) + (53.94)(2.37)] / 100
= 52.00

[2]

Chromium is a transition metal.

(b) (i) Describe the bonding in the element chromium. Draw a diagram to illustrate your answer.

[1]



metallic bonding in chromium the electrostatic attraction between (positive) chromium ions and delocalised (or a sea of) electrons.

(ii) State two physical properties that you would expect chromium metal to possess. Explain, in terms of the bonding present, why it possesses these properties.

[3]

property Good electrical conductivity
explanation delocalised sea of electrons are mobile electrons that can act as charge carriers

property high melting/boiling point

explanation strong electrostatic force of attraction between positive metal ions and sea of delocalised electrons requiring a large amount of energy to break.

(iii) Chromium metal is produced by reducing chromium(III) oxide with aluminium or silicon.

State the full electronic configuration of a chromium atom, Cr and a chromium ion, Cr^{3+}

[2]

Cr $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

Cr^{3+} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

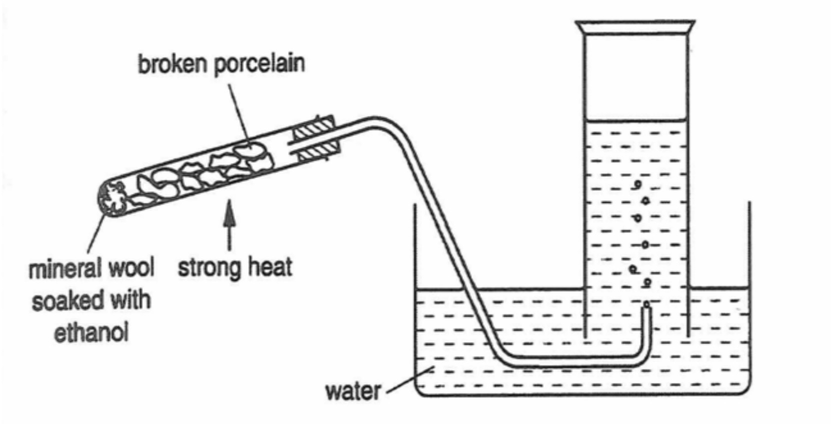
[6]

(c) A student put 5 cm^3 of dilute sulfuric acid in a boiling tube. He added 5 drops of potassium dichromate (VI) solution and then 2 drops of ethanol. He heated the mixture until it just boiled.

(i) What colour change would the student see as he carried out this reaction ?
from orange to green

(ii) Name the organic product formed and the type of reaction that has occurred.
product ethanal / ethanoic acid
type of reaction oxidation

(d) The students then carried out another reaction of ethanol using the apparatus shown in the diagram below. The broken porcelain used contains Al_2O_3.



(i) What is the name of the gas collected in the as jar? ethene

(ii) What type of reaction has the ethanol undergone ? elimination

(e) What reagent and conditions are necessary to convert propanone into propan-2-ol?
$LiAlH_4$ in dry ether, reflux / H_2, Pt / $NaBH_4$ in water or methanol

[Total: 14]

2 Tin forms an oxide, **A**, that contains the metal in both oxidation states II and IV. The formula of **A** can be found by the following method.

• A sample of **A** was dissolved in $H_2SO_4(aq)$, producing solution **B**, which was a mixture of tin(II) sulfate and tin(IV) sulfate.

First titration

• A 25.0 cm^3 sample of solution **B** was titrated with 0.0200 mol dm^{-3} $KmnO_4$.
13.50 cm^3 of $KmnO_4$ was required to reach the end-point.

Second titration

• Another 25.0 cm^3 sample of solution **B** was stirred with an excess of powdered zinc.
This converted all the tin (IV) into tin(II). The excess of zinc powder was filtered off and the filtrate was also titrated with 0.0200 mol dm^{-3} $KmnO_4$, as before.
This time 20.30 cm^3 of $KmnO_4$ was required to reach the end-point.

The equation for the reaction occurring during the titration is as follows.

$$2MnO_4^- + 16H^+ + 5Sn^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 5Sn^{4+}$$

(a) **(i)** Write a balanced ionic equation with state symbols for the reaction between Zn and Sn^{4+}.

$Zn(s) + Sn^{4+}(aq) \longrightarrow Zn^{2+}(aq) + Sn^{2+}(aq)$

(ii) Use the results of the two titrations to calculate

• the number of moles of Sn^{2+} in the first titration sample,

$=13.5/1000 \times 0.0200 \times 5/2 = 6.75 \times 10^{-4}$ mol

• the number of moles of Sn^{2+} in the second titration sample.

$= 20.3/1000 \times 0.0200 \times 5/2 = 1.02 \times 10^{-3}$ mol

(iii) Use the results of your calculation in **(ii)** to deduce the Sn^{2+}/ Sn^{4+} ratio in the oxide **A**, and hence suggest the formula of **A**.

[2]

number of moles of $Sn^{4+} = 1.015 \times 10^{-3} - 6.75 \times 10^{-4} = 3.40 \times 10^{-4}$

Sn^{2+}/ Sn^{4+} ratio = 6.75 / 3.40 = 1.99 / 1 = 2 : 1

$2\ SnO + SnO_2 \longrightarrow Sn_3O_4$

(b) A major use of tin is to make 'tin plate', which is composed of thin sheets of mild steel electroplated with tin, for use in the manufacture of food and drinks cans. A tin coating of 1.0×10^{-5} m thickness is often used.

(i) Calculate the volume of tin needed to coat a sheet of steel 1.0 m x 1.0 m to this thickness, on one side only.

Volume = $1 \times 1 \times 1.0 \times 10^{-5} = 1.0 \times 10^{-5}$ m^3 or **10 cm^3**

(ii) Calculate the number of moles of tin that this volume represents.
[The density of tin is 7.3 g cm^{-3}.]

Mass = vol x density = 10 x 7.3 = 73 g

Number of moles of tin = 73/119 = 0.613 mol

[Total: 9]

3 **(a)** **(i)** Define the term *standard enthalpy change of formation*.

Standard enthalpy change of formation is the heat change when one mole of substance is formed from its constituent elements in their standard states at 298 K and 1 atm.

(ii) Carbon, hydrogen and ethene each burn exothermically in an excess of air.

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^{\theta}_c = -393.7$ kJ mol^{-1}

$H_2(g) + ½O_2(g) \longrightarrow H_2O(l)$ $\Delta H^{\theta}_c = -285.9$ kJ mol^{-1}

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ $\Delta H^{\theta}_c = -1411.0$ kJ mol^{-1}

Write an equation for the standard enthalpy change of formation, $\Delta H^{\theta}{}_f$, of ethene.

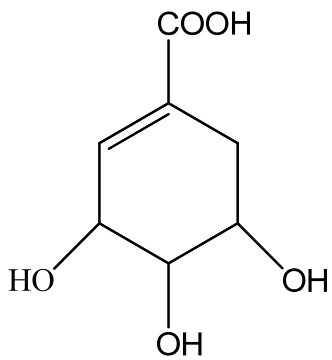
$$2C(s) + 2H_2(g) \longrightarrow C_2H_4(g)$$

Hence, use the data to calculate the standard enthalpy change of formation, $\Delta H^{\theta}{}_f$, in kJ mol^{-1}, of ethene at 298 K.

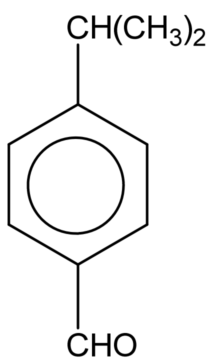
$\Delta H^{\theta}{}_f = 2(-393.7) + 2(-285.9) - (-1411)$
= + 51.8 kJ mol^{-1}

$\Delta H^{\theta}{}_f$ = ………………kJ mol^{-1}
[4]

(b) Shikimic acid and cuminaldehyde are naturally occurring compounds found in the spice plant star anise and the spice cumin respectively.



shikimic acid



cuminaldehyde

(i) Explain why it is suggested that shikimic acid is more soluble in water than cuminaldehyde

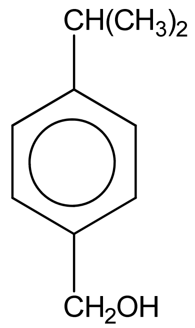
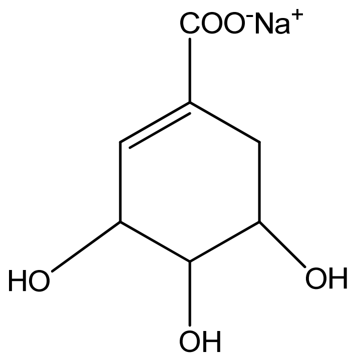
Shikimic acid forms more extensive hydrogen bond with water molecules due to OH groups and COOH group

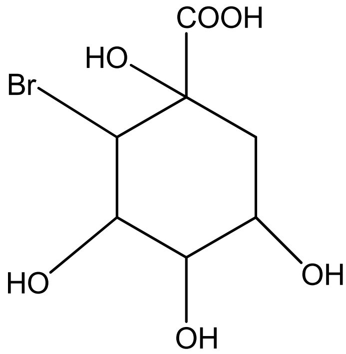
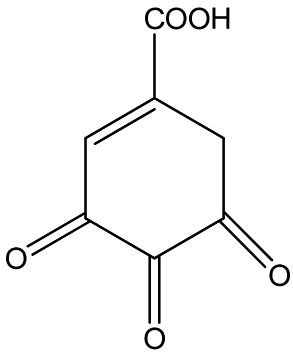
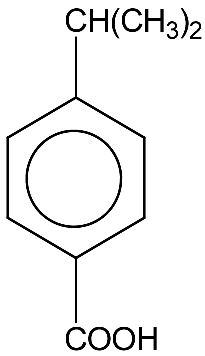
(ii) Explain why shikimic acid is more acidic than alcohol.

The conjugate base carboxylate anion is more stable than OH^- ion due to the resonance effect by C=O
or
Due to electron withdrawing effect of C=O in COOH group on shikimic acid, the O-H in COOG group in shikimic acid is more polarised , hence it releases H^+ more readily than water

[4]

(c) For **each** of the following reagents, draw the structural formula of the product obtained for **each** of the two compounds. If no reaction occurs write ***no reaction*** in the box.

reagent	product with shikimic acid	product with cuminaldehyde
$NaBH_4$(methanol)	No reaction	
NaOH(aq)		No reaction

Br_2(aq)	 Accept swop of positions of OH and Br But do not accept Br and Br as it is a minor product.	No reaction
H_2SO_4 (aq), $K_2Cr_2O_7$ (aq), heat under reflux		

[6]

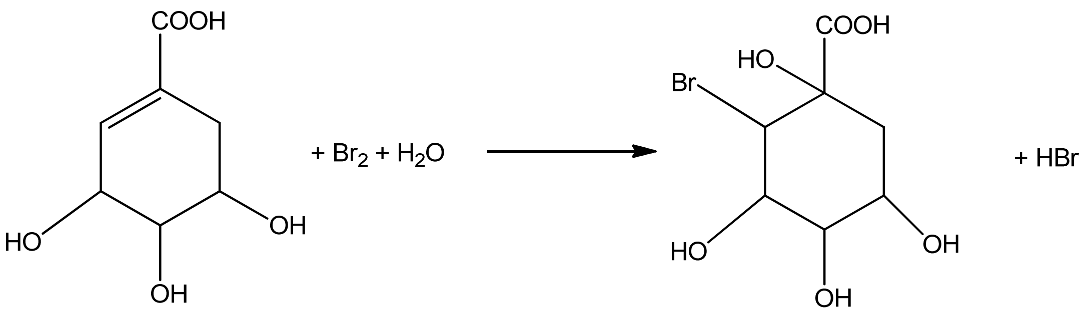
(d) Choose **one** of the above four reagents that could be used to distinguish between shikimic acid and cuminaldehyde. Describe the observations you would make with each compound. Write equation(s) for any reaction(s) that occurs.

reagent Br$_2$ (aq)

observation with cuminaldehyde....reddish brown Br$_2$ remained ......

observation with shikimic acid.........decolourises reddish-brown Br$_2$ ..

Equation:



[3]
[Total : 17]

Section B

Answer **two** questions from this section on separate answer paper

4 **(a)** Define what is meant by a Bronsted base. [1]

A Bronsted base is a substance that is able to accept a H^+ ion from an acid (i.e. proton acceptor)

Or it is a proton, H^+ acceptor.

(b) Carbon dioxide, CO_2, from burning of fossil fuels, is changing the fundamental chemistry of our oceans. When carbon dioxide reacts with water, it forms carbonic acid, H_2CO_3. H_2CO_3 subsequently dissociates into bicarbonate ions, HCO_3^-, and hydrogen ions, H^+, into the sea, lowering pH and causing "acidification" of the ocean.

A solution of 0.100 mol dm^{-3} H_2CO_3 has a pH of 3.68.

Due to the increasing levels of atmospheric CO_2, the oceans have become approximately 30% more acidic (in terms of concentration of H^+ ions) over the last 150 years as the pH of seawater decreases from approximately 8.25 to 8.14.

Chemical species like HCO_3^- and CO_3^{2-} are the essential components of the carbonate buffer system which regulates the pH of seawater. The equilibrium reaction for CO_2 chemistry in seawater that most cogently captures its behaviour is shown below.

$$CO_2 + CO_3^{2-} + H_2O \rightleftharpoons 2\ HCO_3^-$$

The natural pH of the ocean is determined by a need to balance the deposition and burial of $CaCO_3$ on the sea floor against the influx of Ca^{2+} and CO_3^{2-} into the ocean from weathering of limestone rocks and other minerals on land. Coral reefs are built from limestone, $CaCO_3$, by the reaction shown below.

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$$

When CO_2 increases too rapidly, the natural equilibrium of calcium carbonate is upset. This alters the balance of the buffers and gradually allows the oceans to become more acidic.

(i) Explain, with the aid of appropriate calculations, whether carbonic acid, H_2CO_3, is a strong or weak acid. You may assume that carbonic acid, H_2CO_3, to be monoprotic in your calculations.

[2]

$[H^+(aq)]$ from 0.100 mol dm^{-3} H_2CO_3 = $10^{-3.68} = 2.09 \times 10^{-4}$ mol dm^{-3}

Since the concentration of $H^+(aq)$ is less than the concentration of H_2CO_3, H_2CO_3 undergoes partial dissociation.

Hence, H_2CO_3 is a weak acid.

(ii) Calculate the percentage increase in the concentration of H^+ ions in the last 150 years. [2]

Increase in $[H^+(aq)] = 10^{-8.14} - 10^{-8.25}$

$= (7.24 \times 10^{-9}) - (5.62 \times 10^{-9})$ mol dm^{-3}

$= 1.62 \times 10^{-9}$ mol dm^{-3}

Percentage increase in $[H^+(aq)] = \dfrac{1.62 \times 10^{-9}}{5.62 \times 10^{-9}} \times 100\% = 28.8\%$

(iii) With the aid of two balanced equations, show how the carbonate buffer system regulates the pH of the seawater. [2]

Upon addition of small amount of H^+,
$H^+ + CO_3^{2-} \rightarrow HCO_3^-$

Upon addition of small amount of OH^-,
$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$

(iv) Other than increasing levels of atmospheric carbon dioxide gas, suggest another environmental phenomenon that can contribute to ocean acidification. [1]

Acid rain arising from dissolved oxides of nitrogen and SO_2 in the atmosphere.

(c) In an experiment, 20 cm^3 of 1.00 mol dm^{-3} sodium hydrogen carbonate, is added to 10 cm^3 of 1.00 mol dm^{-3} aqueous hydrochloric acid.

(i) Deduce, with appropriate working, which is the limiting reagent.
$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$
no. of moles of $NaHCO_3$ = 0.020 mol
no. of moles of HCl = 0.010 mol
since $NaHCO_3$: HCl = 1 : 1, HCl is the limiting reagent

(ii) If the temperature fell by 3.7°C, calculate the enthalpy change of the reaction. [1]
$q = mc\Delta T$
$q = (30)(4.18)(3.7) = 463.98$ J
$\Delta H = +463.98/0.01 = +46398 = \underline{+46.4 \text{ kJ mol}^{-1}}$

(iii) A student was told that the concentration of hydrochloric acid might not be exactly 1.00 mol dm^{-3}. He decided to carry out titration against a standard solution of sodium hydrogen carbonate to determine the concentration of hydrochloric acid. Suggest an indicator he could use. [1]

methyl orange

(iv) Another student repeated the experiment with 40 cm^3 of 1.00 mol dm^{-3} sodium hydrogen carbonate added to 10 cm^3 of 1.00 mol dm^{-3} aqueous hydrochloric acid, all other experimental conditions are kept constant.

Suggest whether the temperature fall will be above or below 3.7 °C and hence suggest the enthalpy change of the reaction. [2]

Temperature will below 3.7 °C and the enthalpy change of the reaction remains the same.

(d) *Use of the Data Booklet is relevant to this question.*
Part of the Periodic Table is shown below.

Group	I	II		III	IV	V	VI	VII	VIII
	Li	Be		B	C	N	O	F	Ne
Period 3	Na	Mg		Al	Si	P	S	Cl	Ar

From the elements shown in the table, identify the one which exhibits each of the following property. Copy the table to write your answers for (i) to (viii). [7]

(i) Ne	**(ii) P**	**(iii) Be**	**(iv) F**
(v) B	**(vi) C**	**(vii) Al/Si**	**(viii) P/S**

(i) It has the highest first ionisation energy.

(ii) It has the largest ionic radius.

(iii) It has an electronegativity similar to that of aluminium.

(iv) It has a hydride that forms the strongest intermolecular hydrogen bonds.

(v) It has a trifluoride with molecules which has trigonal planar shape.

(vi) It has a chloride that neither reacts with nor dissolves in water.

(vii) It has an oxide with a giant structure and a chloride which is readily hydrolysed in water.

(viii) It has an oxide that produces a strong acid when treated with water.

(ix) Write equations for the reactions for either **(vii)** and **(viii)**.

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_3O^+$

$SiCl_4(l) + 4H_2O(l) \rightarrow Si(OH)_4(s) + 4HCl(l)$

Either one

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

[Total: 20]

5 **(a)** Propanone reacts with iodine in the presence of acid according to the equation

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

A student, Mark, wanted to study the kinetics of the above reaction.

He prepared a mixture containing:

- 5 cm^3 of propanone of concentration 1.0 mol dm^{-3},
- 10 cm^3 of sulfuric acid of concentration 1.0 mol dm^{-3} ,
- 10 cm^3 of a solution of iodine of concentration 1.0×10^{-3} mol dm^{-3}
- 75 cm^3 of distilled water.

At every five minutes interval, 10.0 cm^3 samples were removed and 10 cm^3 of aqueous sodium hydrogencarbonate was added, followed by a titration against a solution of sodium thiosulfate(VI).

The experiment was repeated using 20 cm^3 of sulfuric acid in the reaction mixture, with 65 cm^3 of water to keep total volume constant.

The following results were obtained.

Time/min		5	10	15	20	25
Titre/cm^3	for 10 cm^3 acid (experiment 1)	18.50	17.00	15.50	14.00	12.50
	for 20 cm^3 acid (experiment 2)	17.00	14.00	11.00	8.00	5.00

(i) State the roles of iodine and sulfuric acid in this reaction.

[2]

Iodine – oxidising agent
H_2SO_4 – catalyst

(ii) Explain why sodium hydrogencarbonate was added prior to the titration.

[1]

$NaHCO_3$ added prior to the titration to quench reaction by reacting with the catalyst, H_2SO_4 so that concentration of iodine present at different time intervals can then be found.

(iii) Mark went to plot the graph of titre volume against time for both experiment 1 and 2 on the same graph. He obtained a straight line with a negative gradient for both graph. He also found that the gradient for the experiment 1 was half of the experiment 2.

(I) Using the above information, deduce the order of reaction with respect to iodine and sulfuric acid respectively.

(II) What does the magnitude of gradient represent?

(III) If the experiment was repeated at a higher temperature, how would you expect the magnitude of the gradient to change?

[4]

(I) Zero order wrt iodine
First order wrt sulfuric acid
(with reasoning)

(II) Rate

(III) Magnitude of gradient will increase

(iv) Write a balanced equation for the titration reaction.

[1]

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

(v) Mark found that volume of thiosulfate required was 20.00 cm^3 as he extrapolate the graph to y-axis at t = 0 min in a 10.0 cm^3 reaction mixture. Calculate the concentration of the sodium thiosulfate(VI) solution used in the titration.

[2]

Volume of thiosulfate required = 20.0 cm^3

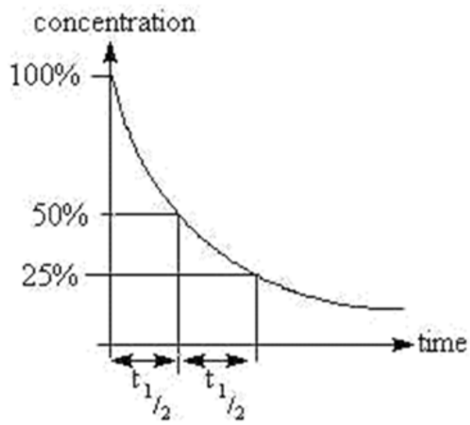
No. of moles of I_2 reacted = 0.01 x 1.0 x 10^{-3} = 1.0 x 10^{-5} mol

No. of moles of thiosulfate required = 1.0 x 10^{-5} x 2 = 2.0 x 10^{-5} mol

Concentration of thiosulfate used = <u>1.00 x 10^{-3} mol dm^{-3}</u>

(vi) Sketch a concentration-time graph for sulfuric acid in this reaction.

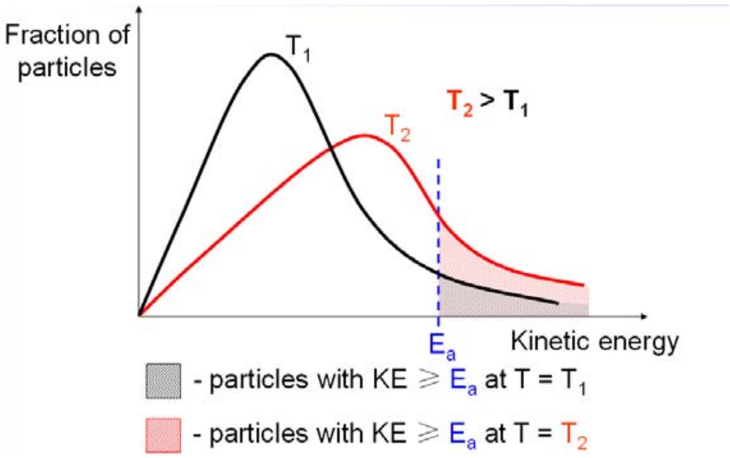
[1]



[must show constant half-life]

(vii) With the aid of a Maxwell-Boltzmann distribution curve, explain how the rate of

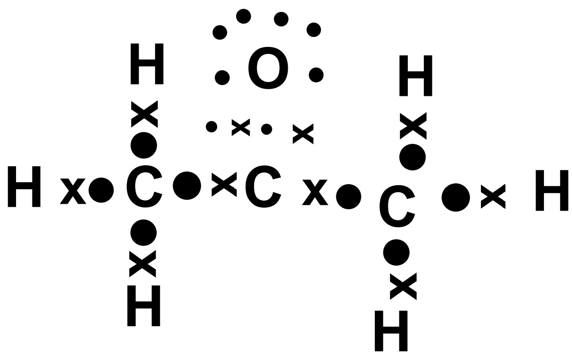
reaction will be affected if the reaction was carried out at a higher temperature.
[4]



[1] for two asymmetric curves starting from origin, correctly labelled with temperature
[1] for labelled axes with single E_a marked out. (2 E_a lose this mark)

At higher temperatures, the kinetic energy of molecules increases. The number of reactant particles with energy ≥ Ea will increase and the frequency of effective collisions increase. Hence the rate of reaction will increase.

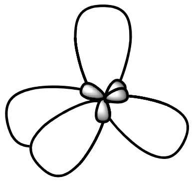
(b) Draw a dot-and-cross diagram for propanone.
[2]



Hence, determine the bond angles in C-C-O and also the H-C-C. **120º, 109.5º**

(c) Describe the bonding of sp^3 carbon in terms of orbital overlap in propanone. Illustrate your answer with a clearly labelled diagram.

[3]



The sp^3 hybridised orbital of the carbon **overlap head-on** with the **s orbital** of each of the three hydrogen atoms to form **sigma bond**.
The sp^3 hybridised orbital of the carbon **overlap head-on** with the **sp^2 hybridised** orbital of the carbon to form a **sigma bond** too.

[Total:20]

6 (a) Nitrogen makes up about 79% of the Earth's atmosphere. As a constituent element of proteins, it is present in living organisms. Oxygen is by far more reactive than nitrogen gas. State one reason why the molecule of nitrogen, N_2 is unreactive. [1]

The N≡N bond is very strong or the N_2 molecule has no polarity.

(b) Lithium reacts readily with nitrogen, and because of this Li_3N has been considered as a possible intermediate in the fixing of nitrogen to make ammonia-based fertilisers.

$$N_2(g) \xrightarrow{+\,Li} Li_3N \xrightarrow{+\,H_2O} NH_3 + \mathbf{A}$$

(i) Construct an equation for the reaction between Li_3N and H_2O and hence identify compound A. [2]

$Li_3N + 3H_2O \rightarrow NH_3 + 3LiOH$

Compound A is LiOH.

(ii) Ammonia is produced in the Haber process. The volume of the reaction vessel is 2 dm^3.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

1 mol of nitrogen and 2 mol of hydrogen are placed in a reaction vessel of 2 dm^3.
After equilibrium is reached, the amount of nitrogen remaining is 0.4 mol.
Write an expression for the equilibrium constant, K_c and calculate the value of K_c for this equilibrium stating its units. [3]

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

	N_2 (g) +	$3H_2$ (g) $\rightleftharpoons$	$2NH_3$ (g)
Initial amt / mol	1	2	0
Change in amt / mol	*-0.6*	*-1.8*	*+1.2*
Equilibrium amt/ mol	0.4	*0.2*	*1.2*
Equilibrium Concentration/ mol dm^{-3}	0.2	*0.1*	*0.6*

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{0.6^2}{0.2 \times 0.1^3} = 1800 \text{ mol}^{-2} \text{ dm}^6$$

(ii) Using your knowledge of the Haber process, state one advantage and one disadvantage of using lithium as a means of fixing nitrogen, rather than the Haber process. [2]

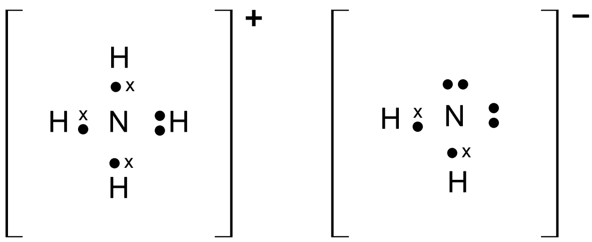
Advantage: No need for high temperature and pressure or catalyst to be used.

Disadvantage: Li is expensive OR Li would need to be removed OR LiOH is strongly basic/ corrosive.

(iii) State one large-scale use for ammonia, other than in the production of fertilisers. [1]
It is used as a refrigerant or explosives or nylon or manufacture of nitric acid.

(iv) Like water, liquid ammonia can also undergo self-ionisation. Write an equation to represent the self-ionisation of liquid ammonia and draw the dot-and-cross diagrams to show the bonding in the species formed. [3]

$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ [1]



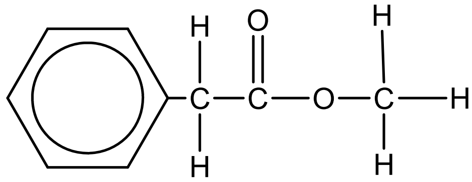
(c) Boron nitride is a heat resistant refractory compound which is made up of boron and nitrogen atoms. It has the chemical formula BN. The hexagonal form corresponds to graphite and is the more stable compound among the BN polymorphs.

(i) Explain the high melting point of boron nitride in terms of its structure and bonding. [2]
Boron nitride has giant covalent structure with strong covalent bonds between atoms. Large amount of energy is needed to break the strong covalent bonds .

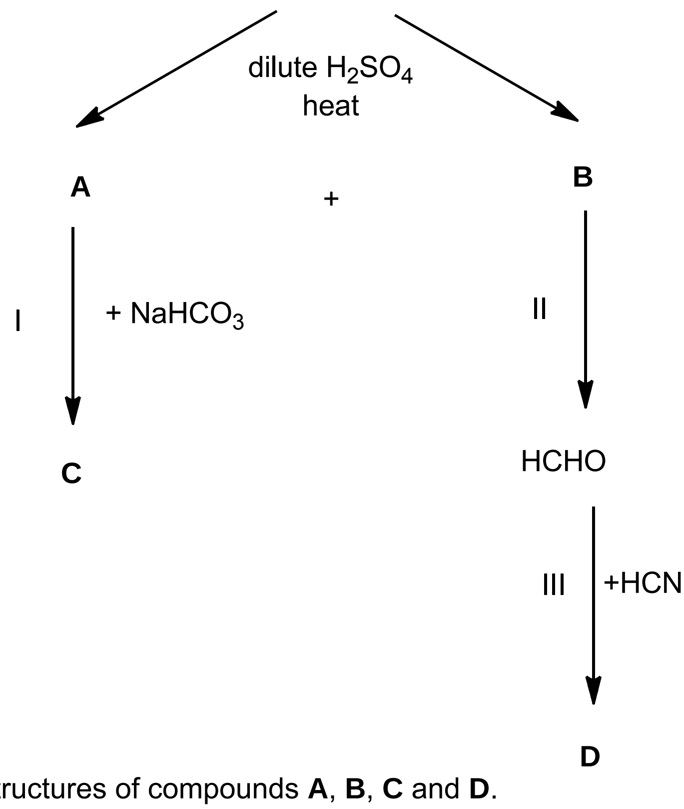
(ii) Suggest a possible industrial use of hexagonal boron nitride. [1]

Lubricant

(d) A sequence of reactions, starting from methyl 2-phenylacetate, is shown below.

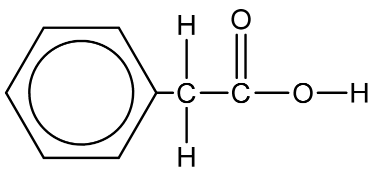


methyl 2-phenylacetate

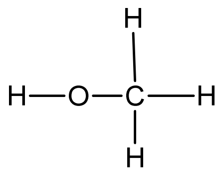


(i) Draw the structures of compounds **A**, **B**, **C** and **D**. [4]

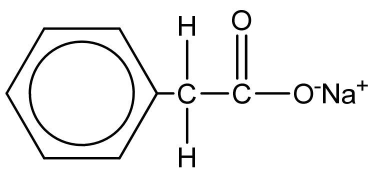
A:



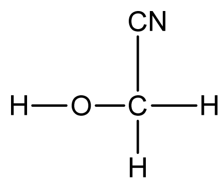
B:



C:



D:



(ii) The aldehyde CH_3CHO can be converted into ethanoic acid. How may this conversion be achieved in a college laboratory? [1]
$KMnO_4$, dilute H_2SO_4,
Heat in a water bath

[Total: 20]